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Journal of Nuclear Materials 324 (2004) 215–219

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Calorimetric measurements on uranium–plutonium mixed oxides

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Received 27 June 2003; accepted 21 October 2003

Abstract

Enthalpy increments of $U_{1-y}Pu_yO_2$ solid solutions with $y = 0.21$, 0.28 and 0.40 were measured using a high-temperature differential calorimeter by employing the method of inverse drop calorimetry in the temperature range 1000–1780 K. From the fit equations for the enthalpy increments, other thermodynamic functions such as heat capacity, entropy and Gibbs energy function have been computed in the temperature range 298–1800 K. The results indicate that the enthalpies of $(U,Pu)O_2$ solid solutions obey the Neumann–Kopp molar additivity rule.

1. Introduction

Mixed uranium–plutonium oxides (MOX) containing about 13–30% PuO_2 have been used as fuels for fast reactors in many countries. Uranium–plutonium mixed oxides containing 21% and 28% PuO_2 have been chosen as fuels for the Prototype Fast Breeder Reactor (PFBR) of India to be constructed. Uranium–plutonium mixed oxides containing 40% and higher amounts of PuO_2 are being considered potential fuels for the plutonium burner reactors [1]. The heat capacity is an important thermodynamic property, which is required for understanding the various chemical interactions likely to occur during the irradiation of the fuel as well as for modeling the behavior of the fuel.

Several experimental data on the heat capacity and enthalpy increments of uranium–plutonium mixed oxides containing 20% and 25% PuO_2 have been reported in the literature [2–9]. In general, there is agreement among different sets of experimental enthalpy increment data within ±3% though the compositions, O/M ratios and temperature ranges are different. The only exceptions are the data of Leibowitz et al. [5,6], which are higher than all the others. There exist correlations by Fink [10,11], Cordfunke and Konings [12], MATPRO [13] and Carbajo et al. [14] for the enthalpy increment and heat capacity data for UO_2, PuO_2 and uranium–plutonium mixed oxides. In the latest correlation, Carbajo et al. [14] recommended the calculation of enthalpy and heat capacity of solid MOX fuel $U_{1-y}Pu_yO_2$ by using the Neumann–Kopp molar additivity rule, since the solid solutions formed in the system UO_2–PuO_2 are almost ideal. They recommended the use of the equations given by Fink for UO_2 [10] and those given by Cordfunke and Konings for PuO_2 [12] because the results are in very good agreement with the experimental data.

No experimental data are available in the literature for the mixed oxides containing 21% and 28% PuO_2, which are the PFBR fuel compositions. Hence, measurements of the enthalpy increments of these oxides were taken up. Further, the conclusion of Carbajo et al. [14] that the solid solutions of mixed oxides obey Neumann–Kopp's law was arrived at from the experimental data of oxides containing 20–30% PuO_2. With a view to verify whether the conclusion holds good also for the solid solutions with higher amounts of plutonium oxides, measurements on the mixed oxides with 40% PuO_2 were also taken up. In this study, measurements of the enthalpy increments of $U_{1-y}Pu_yO_2$ ($y = 0.21$, 0.28 and

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doi:10.1016/j.jnucmat.2003.10.005

0.4) in the temperature range 1000–1780 K were carried out by the inverse drop calorimetry using a high-temperature differential calorimeter. The thermodynamic functions such as heat capacity, entropy and Gibbs energy functions were computed from the measured enthalpy increments.

2. Experimental

2.1. Sample preparation

The $U_{1-y}Pu_yO_2$ ($y = 0.21$, 28 and 40) samples used for the enthalpy increment measurements were prepared, characterised and supplied by Radiometallurgy Division, BARC, Mumbai, India. The experimental procedure used for the preparation and characterisation of uranium–plutonium mixed oxide fuel pellets have been described elsewhere [15]. The characteristics of the mixed oxide samples used in this study are given in Table 1. The lattice parameters are in agreement with the literature data [16]. The total amount of impurities was less than 3000 ppm. Prior to the calorimetric measurements, the mixed oxide samples were equilibrated at 1073 K with an $Ar–H_2/H_2O$ gas mixture having an oxygen potential of $-418.4\ \mathrm{kJ\,mol^{-1}}$ in a gas equilibration set up to make them stoichiometric. No change in the weights of the samples was observed after the measurements and hence the samples have been presumed to have maintained an O/M ratio of 2.00 during the measurements. Further, the enthalpy increment and heat capacity of the mixed oxides do not vary much with the O/M ratio [14].

2.2. Calorimeter

The high-temperature differential calorimeter (Model HT 1500 of M/s. SETARAM, France) used in the present study has been described elsewhere [17]. For carrying out calorimetric measurements on radioactive samples, the calorimeter has been attached to an argon atmosphere glove box, maintained at a negative pressure of 25 mm WG with respect to the ambient. The argon atmosphere radioactive glove box to which the calorimeter is attached has been described elsewhere [18].

2.3. Experimental procedure

The enthalpy increments of $U_{0.79}Pu_{0.21}O_2$ (MOX1), $U_{0.72}Pu_{0.28}O_2$ (MOX2), and $U_{0.60}Pu_{0.40}O_2$ (MOX3) were determined by inverse drop calorimetric technique employing the sandwich method. Each uranium–plutonium mixed oxide sample was dropped from the ambient to experimental temperature, between two α-alumina (SRM 720) reference samples supplied by NIST, USA. The experimental procedure adopted for measuring the enthalpy increment of the sample by the sandwich method has been described earlier [17].

3. Results

The enthalpy increments of $U_{0.79}Pu_{0.21}O_2$ (MOX1), $U_{0.72}Pu_{0.28}O_2$ (MOX2), and $U_{0.60}Pu_{0.40}O_2$ (MOX3) were measured in the temperature range of 1011–1776, 1009–1771 and 1025–1771 K, respectively. They were fitted to 4-term polynomial functions in temperature using the least-squares method. The fitted enthalpy equations for $U_{1-y}Pu_yO_2$ ($y = 0.21$, 28 and 40) over the temperature range from 298 to 1800 K are given below:

$U_{0.79}Pu_{0.21}O_2$ (MOX1):

$$H_T^0 - H_{298}^0/\mathrm{kJ\,mol^{-1}} = 79.895(T/\mathrm{K}) + 3.905 \times 10^{-3}(T/\mathrm{K})^2 + 16 \times 10^5(\mathrm{K}/T) - 29\,534, \quad (1)$$

$U_{0.72}Pu_{0.28}O_2$ (MOX2):

$$H_T^0 - H_{298}^0/\mathrm{kJ\,mol^{-1}} = 77.841(T/\mathrm{K}) + 5.606 \times 10^{-3}(T/\mathrm{K})^2 + 14.917 \times 10^5(\mathrm{K}/T) - 28\,710, \quad (2)$$

$U_{0.60}Pu_{0.40}O_2$ (MOX3):

$$H_T^0 - H_{298}^0/\mathrm{kJ\,mol^{-1}} = 78.263(T/\mathrm{K}) + 5.881 \times 10^{-3}(T/\mathrm{K})^2 + 15.166 \times 10^5(\mathrm{K}/T) - 28\,944. \quad (3)$$

The following constraints were used for fitting the data: (a) $H_T^0 - H_{298}^0 = 0$ at 298 K and (b) the derivative of the function at 298 K is equal to the value of heat capacity of the solid solutions at 298 K ($C_{p,298}^0$) which was estimated from the literature data [14] for $C_{p,298}^0$ of pure UO_2 and PuO_2 using Neumann–Kopp's molar

Table 1
Characteristics of the mixed oxide samples

No.	Sample description	Sintered density in % th.d.	O/M ratio of as prepared sample	Lattice parameter of as prepared sample in pm
1	$U_{0.79}Pu_{0.21}O_2$	96.33	1.96	545.10 ± 0.25
2	$U_{0.72}Pu_{0.28}O_2$	95.63	1.945	544.78 ± 0.39
3	$U_{0.60}Pu_{0.40}O_2$	95.72	1.92	543.96 ± 0.29

additivity rule. The equations fit the enthalpy increment data very well. The standard errors of the fit were 1.24%, 0.67% and 1.35%, respectively. The measured values of the enthalpy increments for MOX1, MOX2 and MOX3 are given in Tables 2–4, respectively. From our fit equations, the values of other thermodynamic functions, namely, heat capacity, entropy and Gibbs energy functions in the temperature range 298–1800 K were computed and these values are also given in Tables 2–4. The S^0_{298} values needed for the computation of the entropy

Table 2
Thermodynamic functions of $U_{0.79}Pu_{0.21}O_2$ (MOX1)

T (K)	$H^0_T - H^0_{298}$ (kJ mol^{-1})		T (K)	$H^0_T - H^0_{298}$ (kJ mol^{-1})	C^0_p (J K^{-1} mol^{-1})	S^0_T (J K^{-1} mol^{-1})	$-(G^0_T - H^0_{298})/T$ (J K^{-1} mol^{-1})
	Measured	From fit					
1011	58.13	56.81	298.15	0	64.225	74.71	74.71
1097	63.27	64.27	300	0.12	64.46	75.11	74.71
1129	67.91	67.06	400	7.05	73.02	94.99	77.36
1193	71.91	72.68	500	14.59	77.40	111.79	82.62
1241	77.71	76.92	600	22.48	80.14	126.16	88.71
1317	84.60	83.68	700	30.59	82.10	138.67	94.97
1389	89.89	90.13	800	38.88	83.64	149.74	101.14
1430	94.59	93.82	900	47.31	84.95	159.67	107.10
1501	97.41	100.25	1000	55.87	86.11	168.68	112.81
1558	105.73	105.45	1100	64.53	87.17	176.94	118.27
1627	110.74	111.78	1200	73.30	88.16	184.56	123.48
1695	117.20	118.05	1300	82.16	89.10	191.66	128.46
1776	127.78	125.58	1400	91.12	90.01	198.29	133.21
			1500	100.16	90.90	204.53	137.76
			1600	109.30	91.77	210.43	142.12
			1700	118.52	92.62	216.02	146.30
			1800	127.82	93.46	221.34	150.33

Table 3
Thermodynamic functions of $U_{0.72}Pu_{0.28}O_2$ (MOX2)

T (K)	$H^0_T - H^0_{298}$ (kJ mol^{-1})		T (K)	$H^0_T - H^0_{298}$ (kJ mol^{-1})	C^0_p (J K^{-1} mol^{-1})	S^0_T (J K^{-1} mol^{-1})	$-(G^0_T - H^0_{298})/T$ (J K^{-1} mol^{-1})
	Measured	From fit					
1009	57.09	57.02	298.15	0	64.403	73.95	73.95
1053	61.14	60.89	300	0.12	64.63	74.35	73.95
1081	63.57	63.37	400	7.05	73.00	94.24	76.61
1107	65.99	65.68	500	14.60	77.48	111.05	81.86
1143	69.05	68.89	600	22.50	80.42	125.45	87.94
1186	73.14	72.75	700	30.66	82.65	138.02	94.23
1214	74.86	75.28	800	39.02	84.48	149.18	100.41
1258	79.17	79.27	900	47.55	86.09	159.23	106.40
1269	80.70	80.27	1000	56.23	87.56	168.37	112.15
1313	84.46	84.30	1100	65.05	88.94	176.79	117.65
1341	86.42	86.87	1200	74.01	90.26	184.58	122.90
1373	89.52	89.82	1300	83.10	91.53	191.86	127.93
1414	93.11	93.62	1400	92.32	92.78	198.69	132.74
1460	96.17	97.91	1500	101.66	93.99	205.13	137.36
1491	100.77	100.81	1600	111.12	95.19	211.23	141.78
1543	105.73	105.71	1700	120.70	96.39	217.04	146.04
1565	108.71	107.79	1800	130.40	97.56	222.58	150.14
1595	111.85	110.64					
1633	113.72	114.27					
1651	116.16	115.99					
1697	120.63	120.41					
1737	123.96	124.27					
1771	127.65	127.57					

Table 4
Thermodynamic functions of $U_{0.60}Pu_{0.40}O_2$ (MOX3)

T (K)	$H_T^0 - H_{298}^0$ (kJ mol^{-1})		T (K)	$H_T^0 - H_{298}^0$ (kJ mol^{-1})	C_p^0 (J K^{-1} mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J K^{-1} mol^{-1})
	Measured	From fit					
1025	57.62	58.93	298.15	0	64.708	72.64	72.64
1071	64.38	63.04	300	0.12	64.94	74.04	72.64
1099	66.13	65.55	400	7.09	73.49	93.05	75.31
1121	67.27	67.53	500	14.69	78.08	109.98	80.60
1160	70.43	71.06	600	22.66	81.11	124.50	86.73
1203	75.53	74.98	700	30.89	83.40	137.18	93.05
1226	77.06	77.08	800	39.33	85.30	148.44	99.29
1271	80.54	81.22	900	47.94	86.98	158.59	105.32
1331	86.25	86.78	1000	56.72	88.51	167.83	111.12
1355	87.94	89.02	1100	65.64	89.95	176.34	116.66
1387	91.07	92.01	1200	74.70	91.32	184.22	121.97
1427	94.18	95.78	1300	83.90	92.66	191.59	127.04
1455	100.32	98.42	1400	93.23	93.96	198.50	131.90
1477	102.00	100.51	1500	102.69	95.23	205.02	136.56
1512	104.68	103.84	1600	112.28	96.49	211.21	141.04
1558	108.32	108.24	1700	121.99	97.73	217.10	145.34
1598	112.20	112.09	1800	131.83	98.97	222.72	149.48
1643	118.88	116.44					
1687	120.22	120.72					
1725	124.38	124.44					
1771	127.02	128.96					

values were also estimated from the literature data [10] for the S_{298}^0 values of UO_2 and PuO_2 using Neumann–Kopp's rule, as was done for the $C_{p,298}^0$ values.

4. Discussion

As can be seen from the tables, the enthalpy increment values for the three compositions are indistinguishable within the experimental uncertainties. The present data are in agreement with the literature data within ±2%, except those of Leibowitz et al. [5,6], which are higher than the other literature data as well. The present enthalpy data for MOX1 are in very good agreement with that for MOX1 computed by using the equations of Carbajo et al. [14] within 0.5%. Similarly the present data for MOX2 and MOX3 are in agreement with those of Carbajo et al. [14] within 1.7%, the agreement being still better below 1300 K. The agreement between the present heat capacity data and those of Carbajo et al. [14] is within 2% for MOX1 and between 2% and 4% for MOX2 and MOX3.

5. Conclusion

Enthalpy increments of uranium–plutonium mixed oxides, $U_{0.79}Pu_{0.21}O_2$, $U_{0.72}Pu_{0.28}O_2$ and $U_{0.60}Pu_{0.40}O_2$ have been measured in the temperature range 1000–1780 K for the first time by inverse drop calorimetry. Other thermodynamic functions, namely, heat capacity, entropy and Gibbs energy functions were computed in the temperature range 298–1800 K. The results indicate that the enthalpies of $(U,Pu)O_2$ solid solutions in the temperature range 298–1800 K obey the Neumann–Kopp molar additivity rule. The present study provides the first experimental thermodynamic data for uranium–plutonium mixed oxides containing 21%, 28% and 40% plutonium oxide, which are in excellent agreement with the recommended thermodynamic data for the mixed oxides.

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